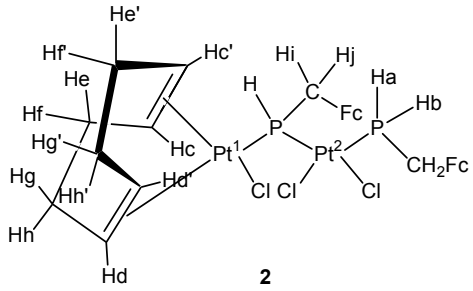
ELECTRONIC SUPPLEMENTARY INFORMATION

Reactivity of mononuclear Pd(II) and Pt(II) complexes containing the primary phosphane (ferrocenylmethyl)phosphane towards metal chlorides and PPh_3.

Maria Michela Dell'Anna[a], Piero Mastrorilli[a*], Cosimo Francesco Nobile[a], Beatrice Calmuschi-Cula[b], Ulli Englert[b], Maurizio Peruzzini[c]



2

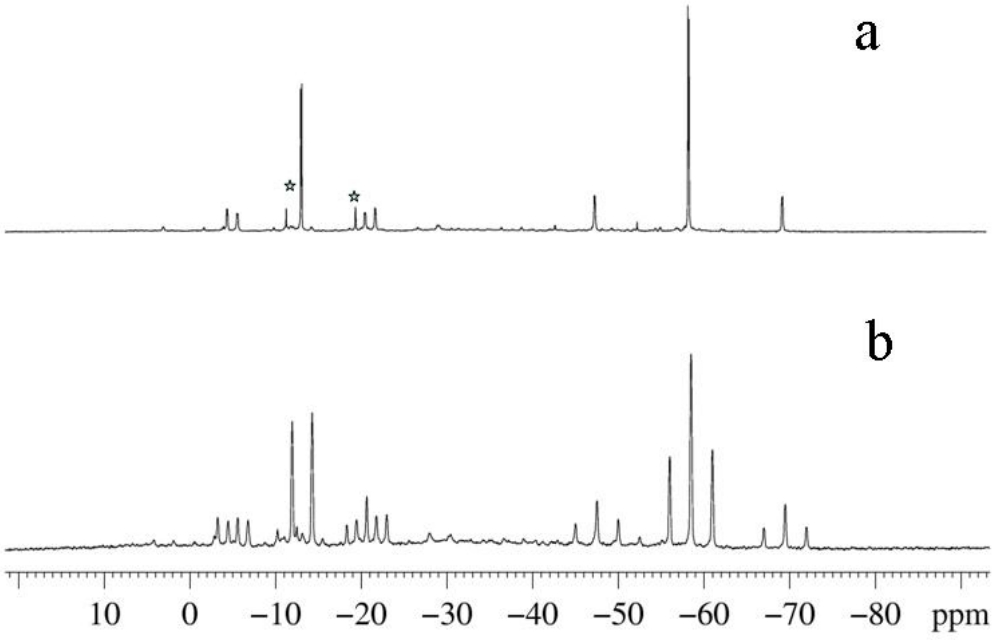


Figure S1: (a) $^{31}P\{^{1}H\}$ and (b) ^{31}P NMR spectra of **2** (CD_2Cl_2, 273 K, 162 MHz). The starred peaks are due to impurities.

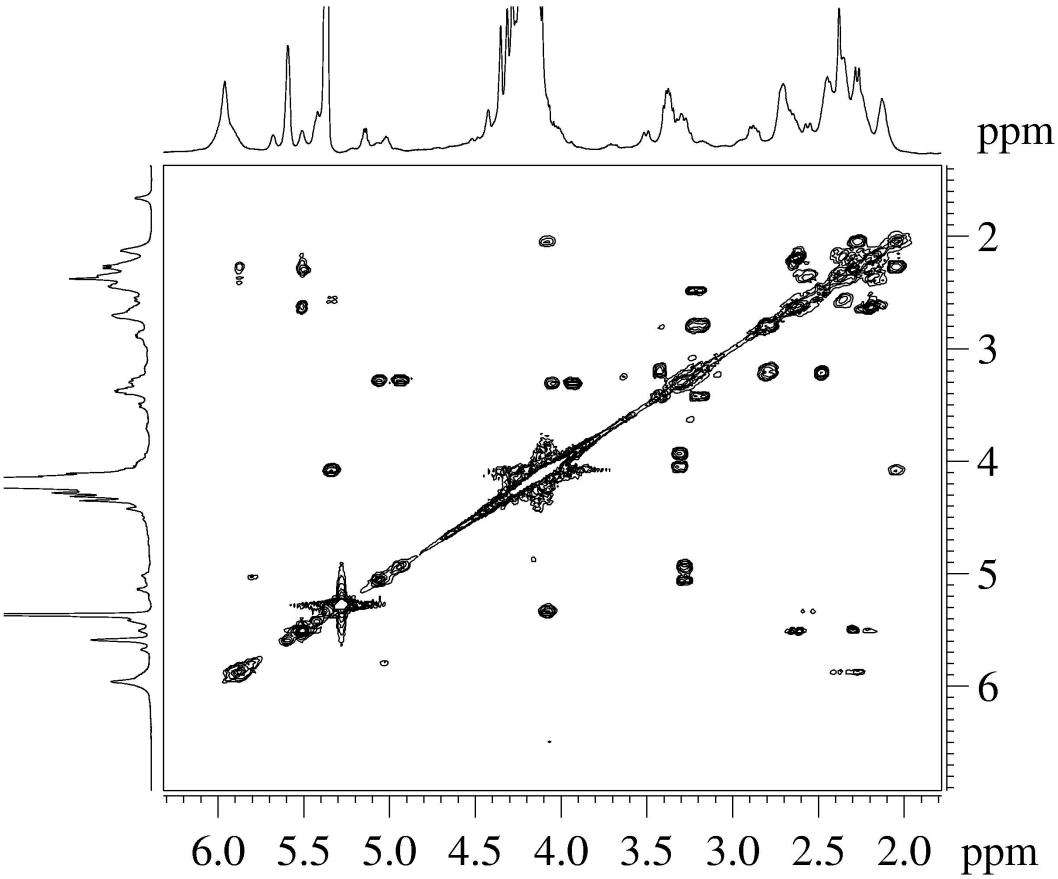


Figure S2: ^{1}H-COSY spectrum of **2** (CD_2Cl_2, 273 K, 400 MHz).

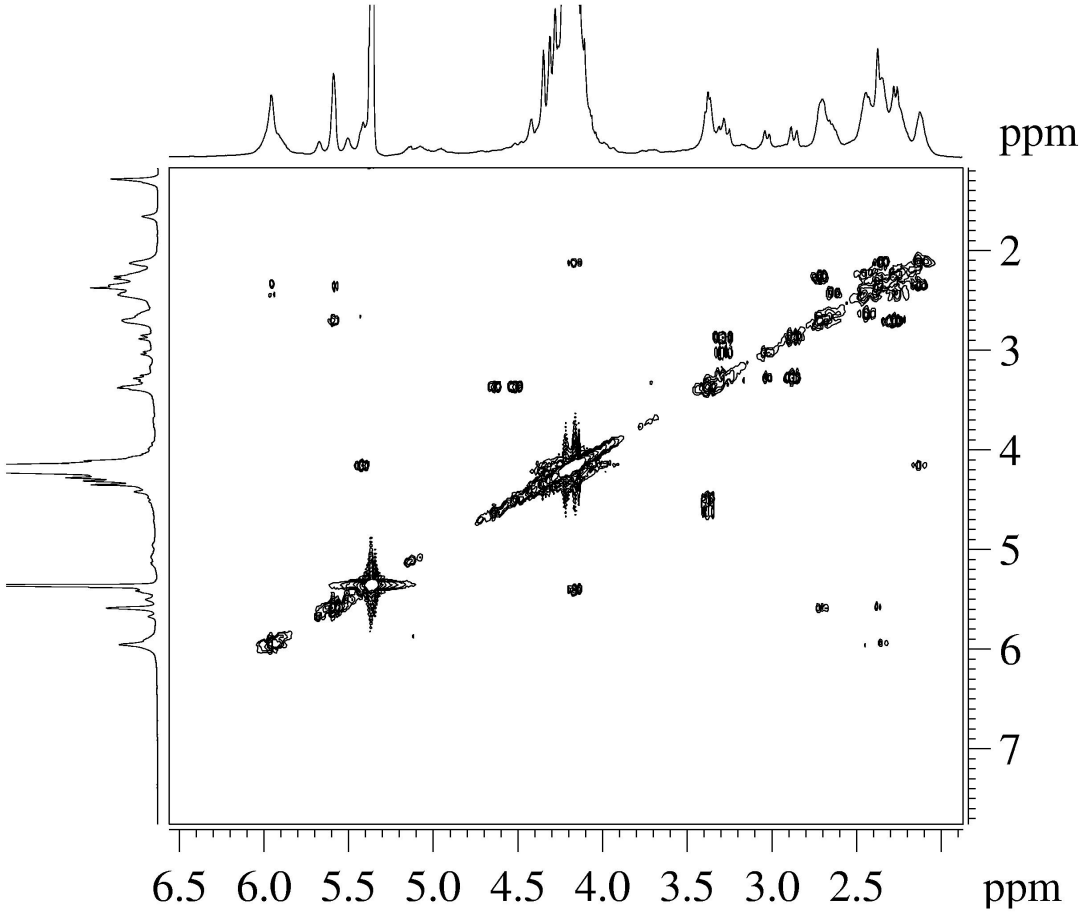


Figure S3: $^{1}H\{^{31}P\}$-COSY spectrum of **2** (CD_2Cl_2, 273 K, 400 MHz).

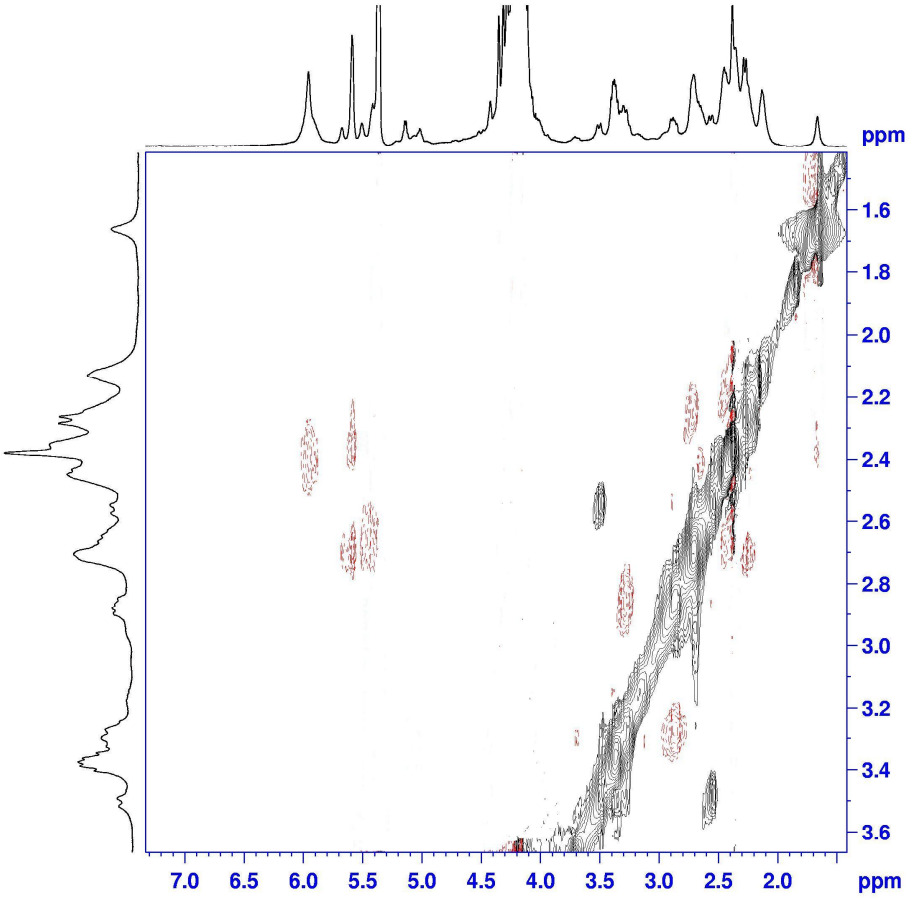


Figure S4: portion of the ^{1}H-NOESY spectrum of **2** (CD_2Cl_2, 273 K, 400 MHz): the red cross peaks indicate *noesy* interaction.

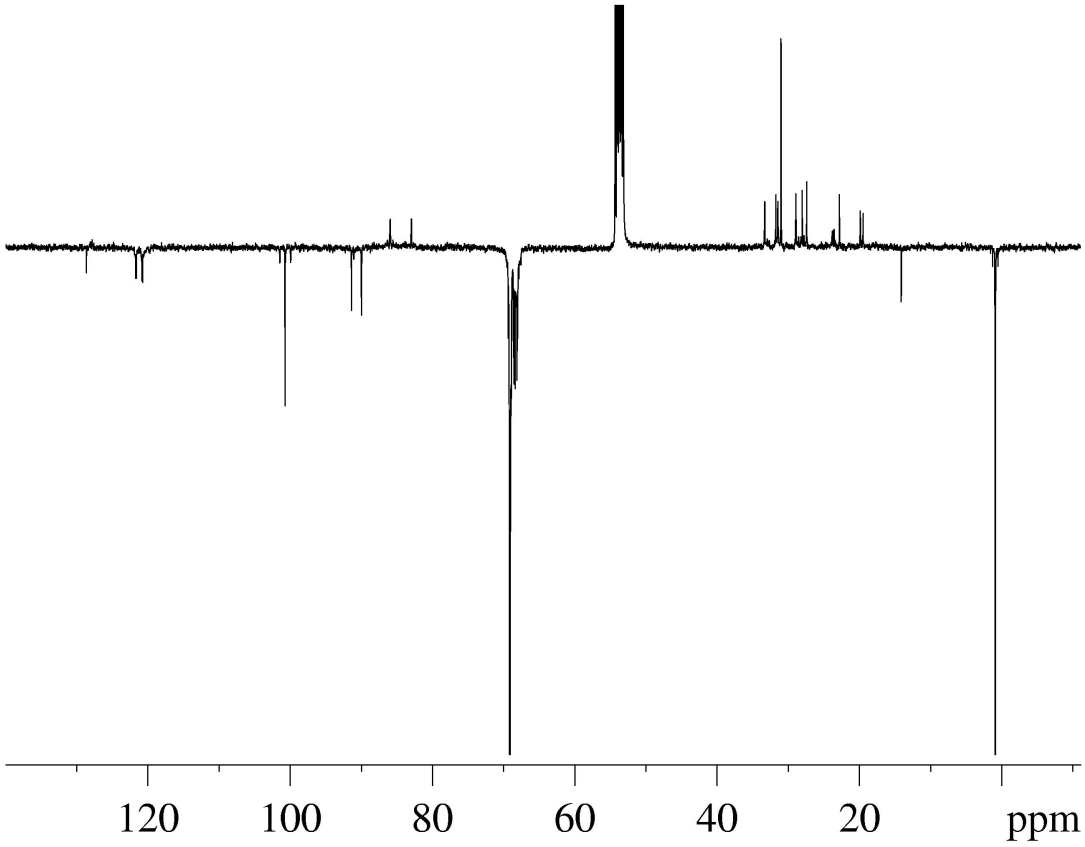


Figure S5: $^{13}C\{^{1}H\}$APT NMR spectrum of **2** (CD_2Cl_2, 273 K, 100 MHz, *C* and *C*H_2 point upward, *C*H and *C*H_3 point downward).

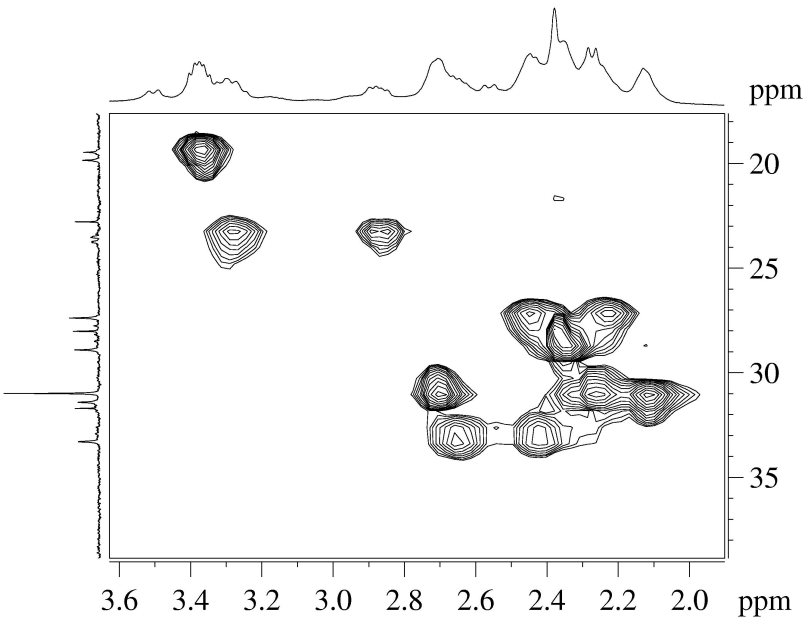


Figure S6: portion of the ^{1}H-^{13}C HMQC spectrum of complex **2** in the methylenic region (CD_2Cl_2, 273 K).

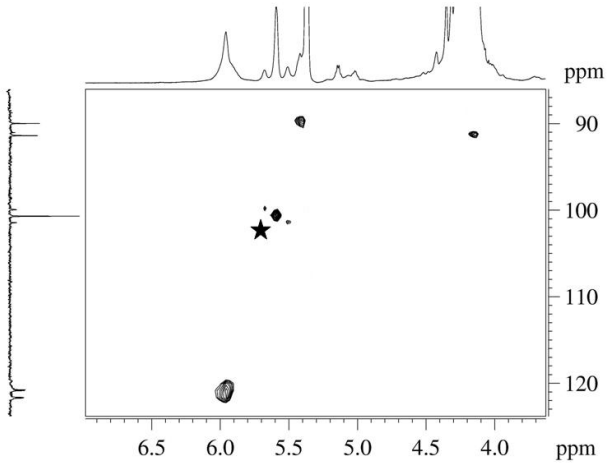


Figure S7: Portion of the ^{1}H-^{13}C HMQC spectrum of **2** in the vinylic region (CD_2Cl_2, 273 K). In the $^{13}C\{^{1}H\}$ APT NMR spectrum of F1 the signals of primary and tertiary carbons point downward. The starred cross peak is due to the [Pt(cod)Cl_2] impurity.

$^{13}C\{^{1}H\}$-APT and ^{1}H-^{13}C HMQC spectra of **2** (Figure S5-7) show the magnetic inequivalence of the four vinylic carbon nuclei.

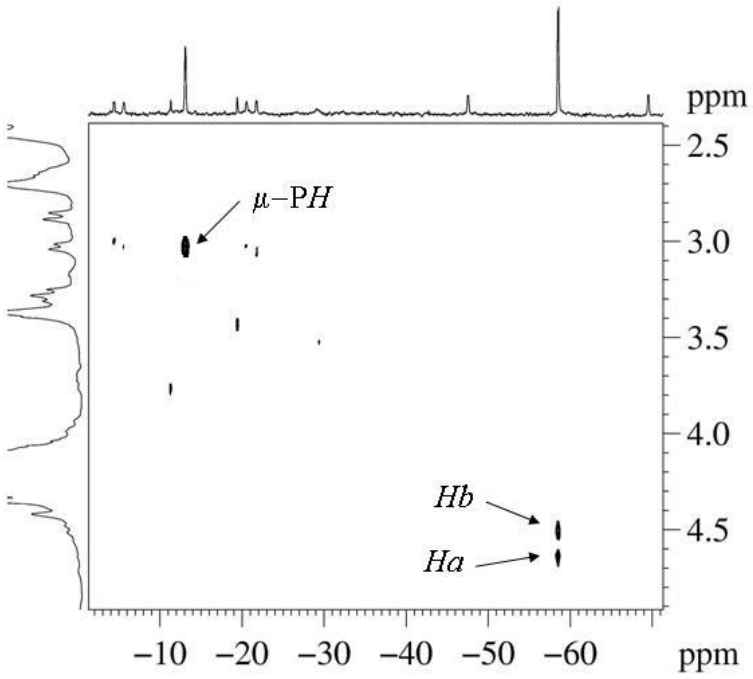


Figure S8: ^{31}P-^{1}H HETCOR spectrum of **2** (CD_2Cl_2, 273 K). The projection on F1 is the ^{1}H{^{31}P} NMR spectrum.

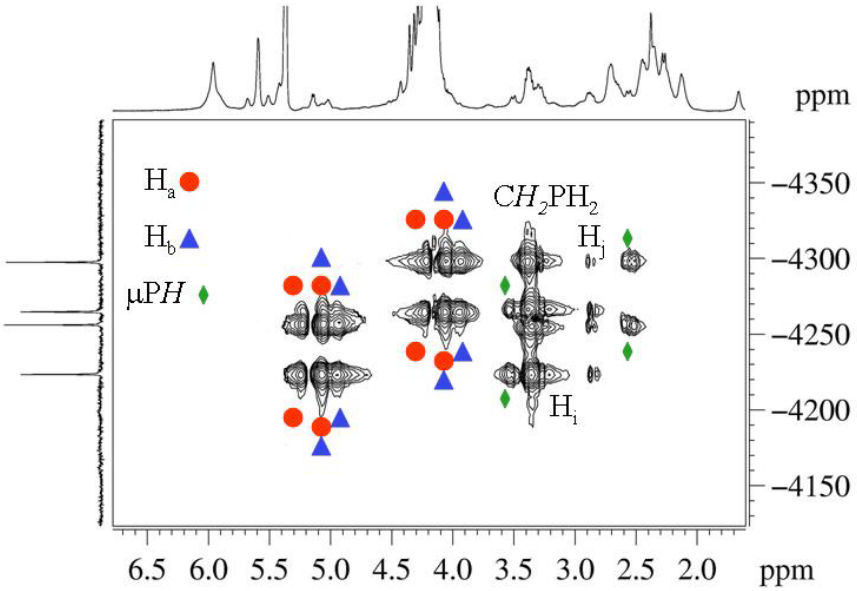


Figure S9: Portion of the ^{1}H-^{195}Pt HMQC spectrum of **2** (CD_2Cl_2, 273 K, Pt^2 region).

The ^{1}H-^{195}Pt HMQC spectrum of **2** in Figure S9 shows that the four different vinylic protons of the coordinated diene couple only with Pt^1 (H_d and $H_{d'}$, $\delta_{Hd'} = \delta_{Hd} = 5.86$, $^{2}J_{Hd\text{-}Pt1} = {}^{2}J_{Hd'\text{-}Pt1} = 40$ Hz; $H_{c'}$, $\delta_{Hc'} = 5.33$, $^{2}J_{Hc'\text{-}Pt1} = 72$ Hz; H_c, $\delta_{Hc} = 4.06$, $^{2}J_{Hc'\text{-}Pt1} = 77$ Hz). The chemical shifts of the diastereotopic vinylic protons *cis* to the phosphido bridging ligand (H_c and $H_{c'}$) are significantly different; on the contrary, the chemical shifts of the diastereotopic vinylic protons *trans* to the phosphido bridging ligand (H_d and $H_{d'}$) are coincident.

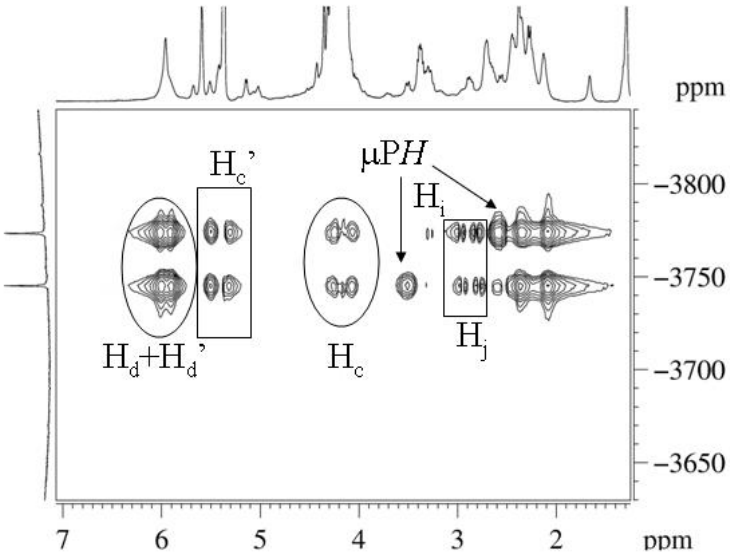


Figure S10: Portion of the ^{1}H-^{195}Pt HMQC spectrum of **2** (CD_2Cl_2, 273 K, Pt^1 region).

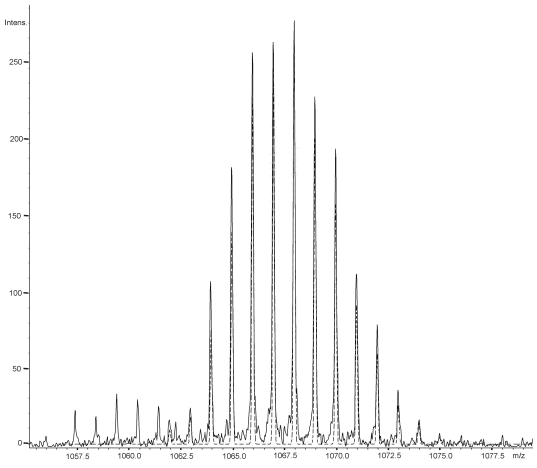
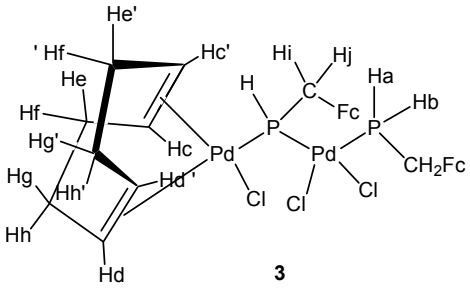


Figure S11: Experimental (solid line) and simulated (dashed line) HRMS(+) spectrum of **2** (exact mass = 1065.9425 da) in THF diluted with CH_3CN. The error between simulated and observed isotopic patterns is –0.9 ppm.



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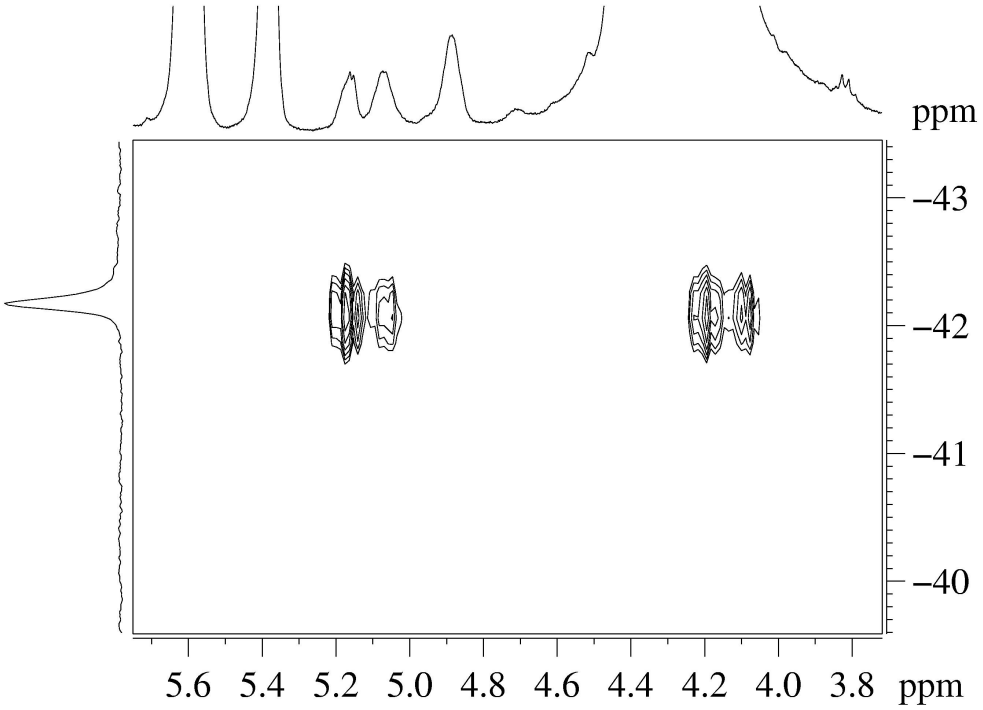


Figure S12: portion of the ^{1}H-^{31}P HMQC spectrum of **3** (CD_2Cl_2, 265 K) in the terminal phosphane region.

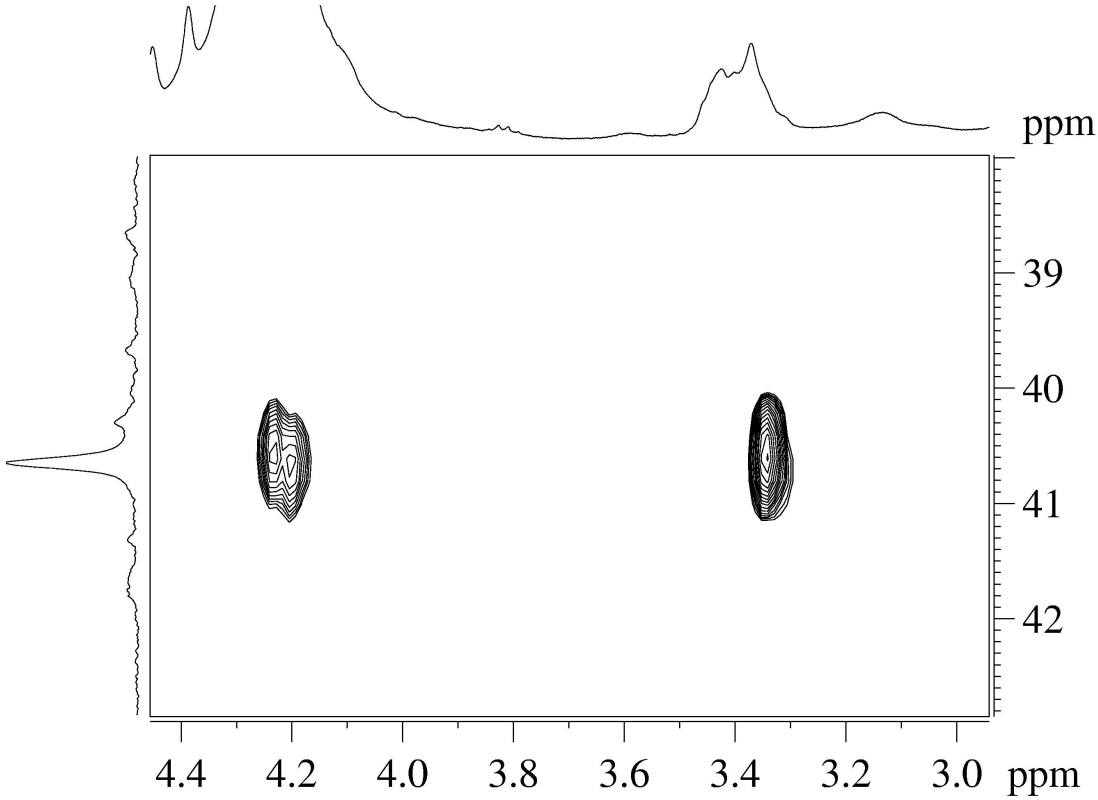


Figure S13: portion of the ^{1}H-^{31}P HMQC spectrum of **3** (CD_2Cl_2, 265 K) in the phosphido-bridged region.

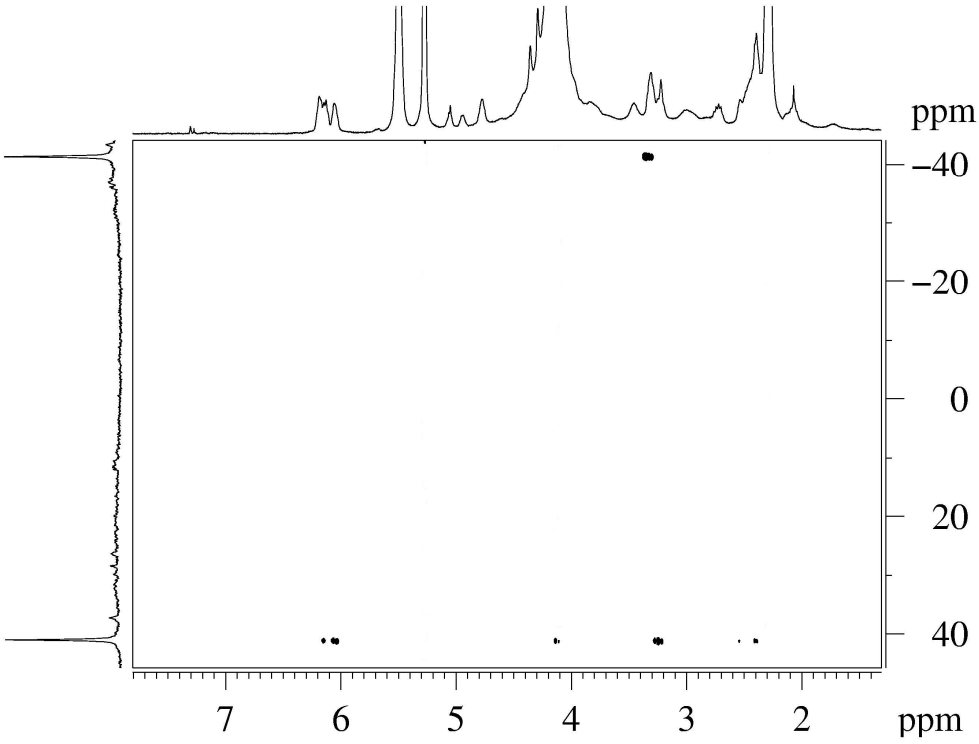


Figure S14: ^{1}H-^{31}P HMBC spectrum of **3** (CD_2Cl_2, 265 K).

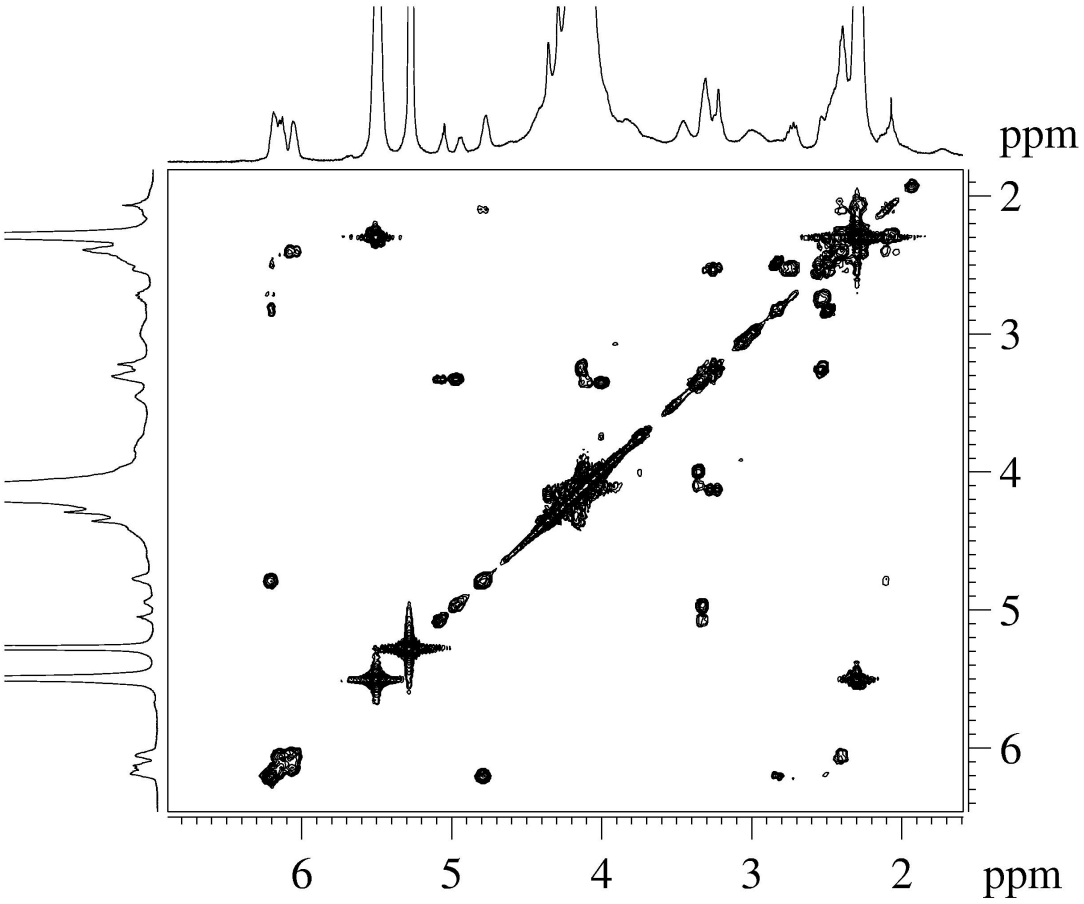


Figure S15: ^{1}H-COSY spectrum of **3** (CD_2Cl_2, 265 K, 400 MHz).

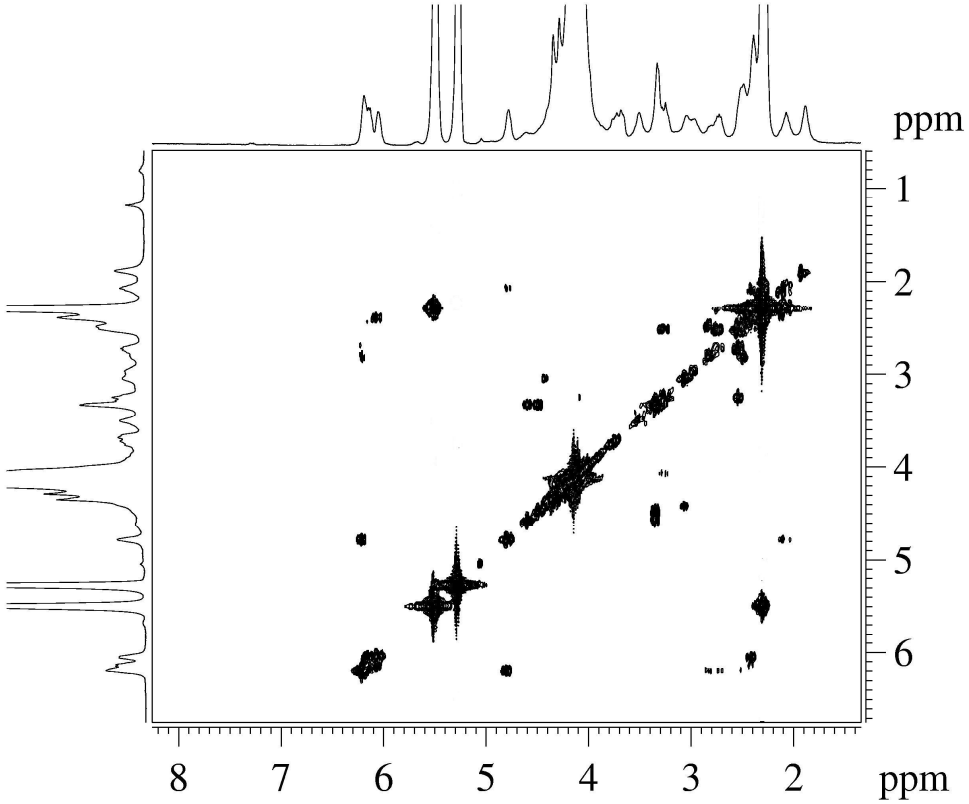


Figure S16: $^{1}H\{^{31}P\}$-COSY spectrum of **3** (CD_2Cl_2, 265 K, 400 MHz).

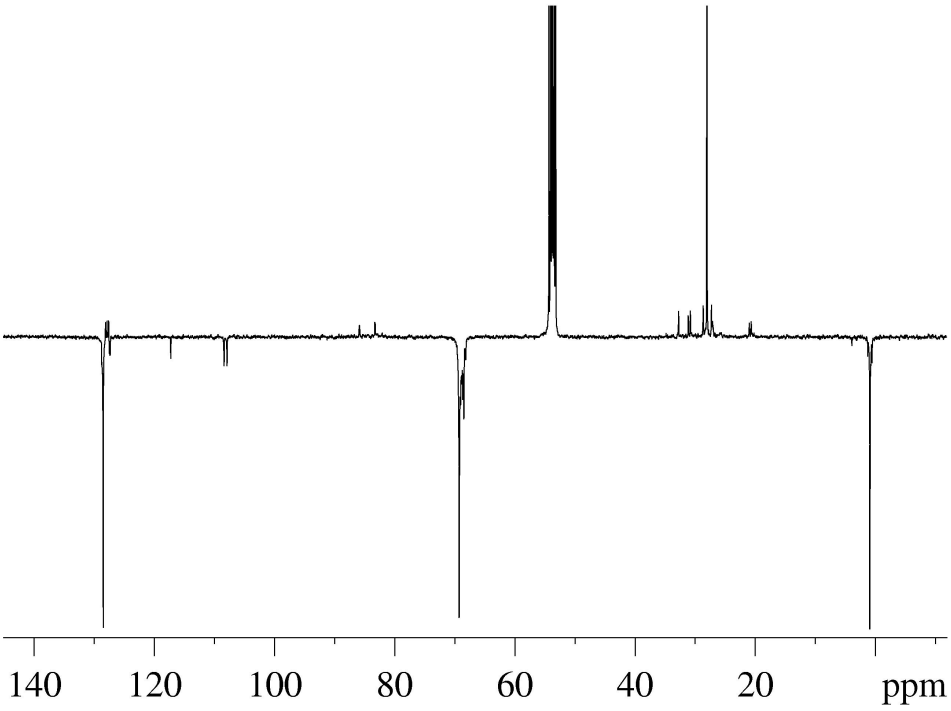


Figure S17: $^{13}C\{^{1}H\}$APT NMR spectrum of **3** (CD_2Cl_2, 265 K, 100 MHz, *C* and *C*H_2 point upward, *C*H and *C*H_3 point downward).

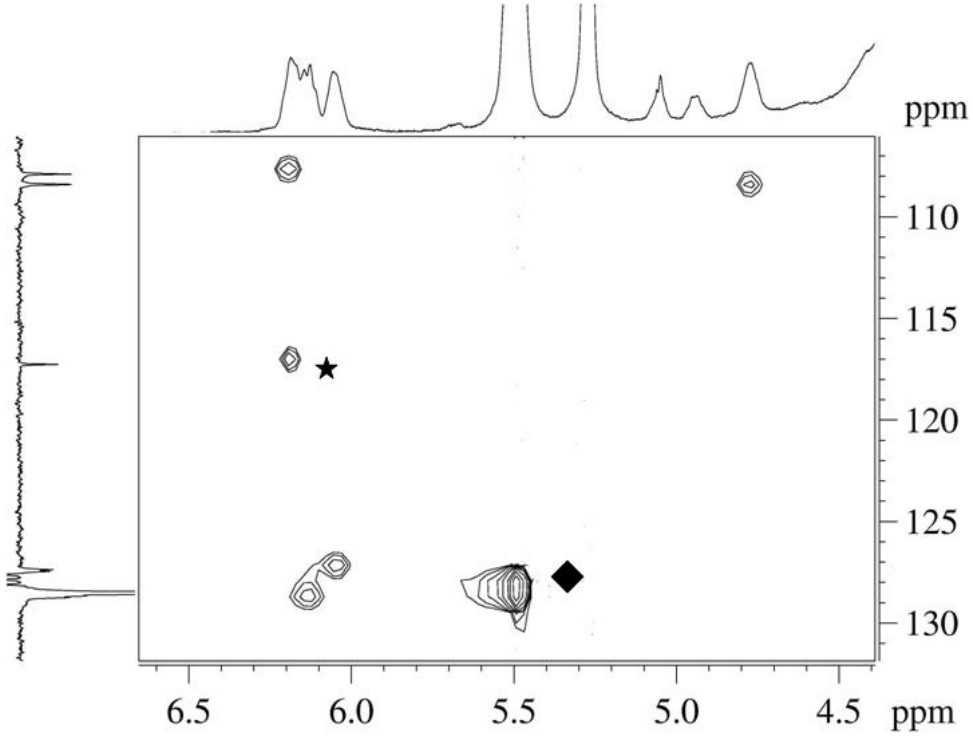


Figure S18: Portion of the ^{1}H-^{13}C HMQC spectrum of complex **3** in the vinylic region (CD_2Cl_2, 265 K). In the reported $^{13}C\{^{1}H\}$ APT NMR spectrum (F1) the signals of primary and tertiary carbons point downward. The cross-peaks marked with the star and with the rhomb are due to the vinylic protons of [Pd(cod)Cl_2] and of free COD impurities, respectively.

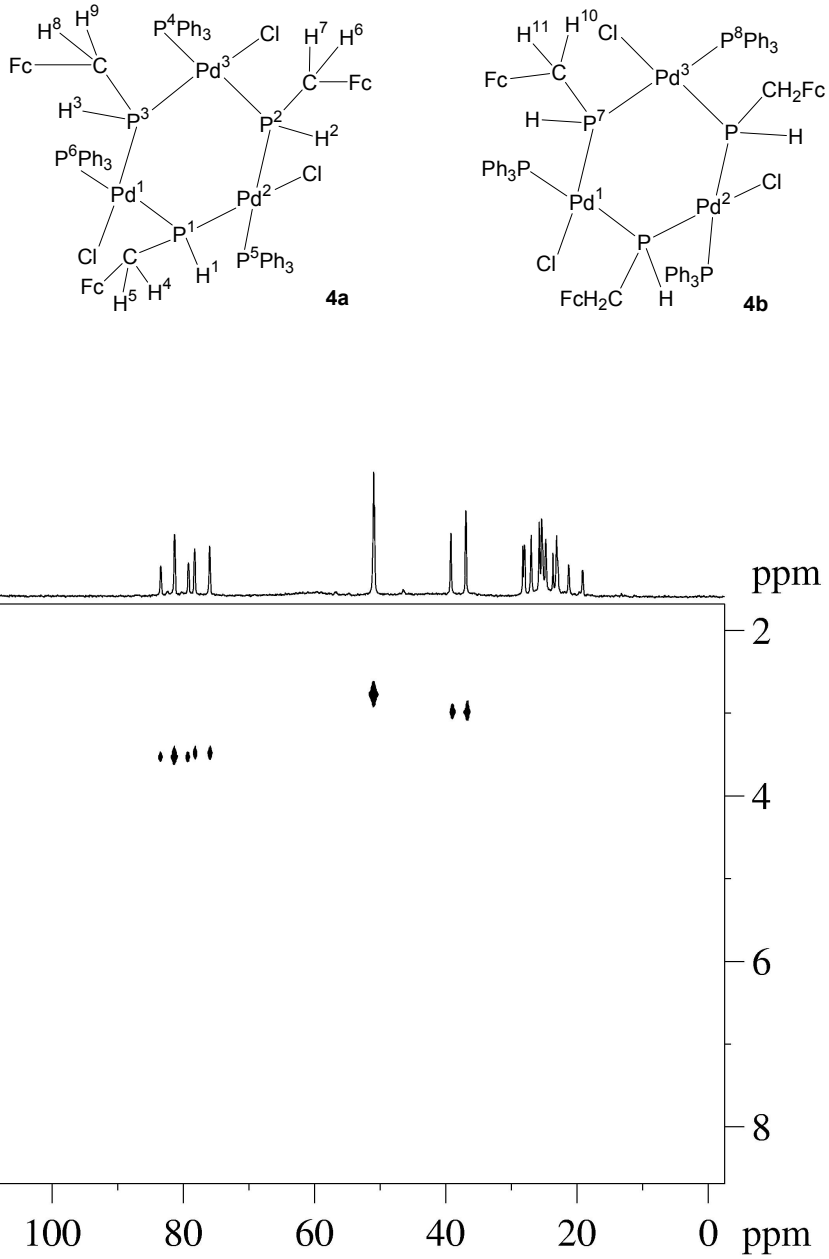


Figure S19: ^{31}P-^{1}H HETCOR spectrum of **4a** and **4b** (CD_2Cl_2, 295 K). The projection on F1 is the $^{1}H\{^{31}P\}$ NMR spectrum.

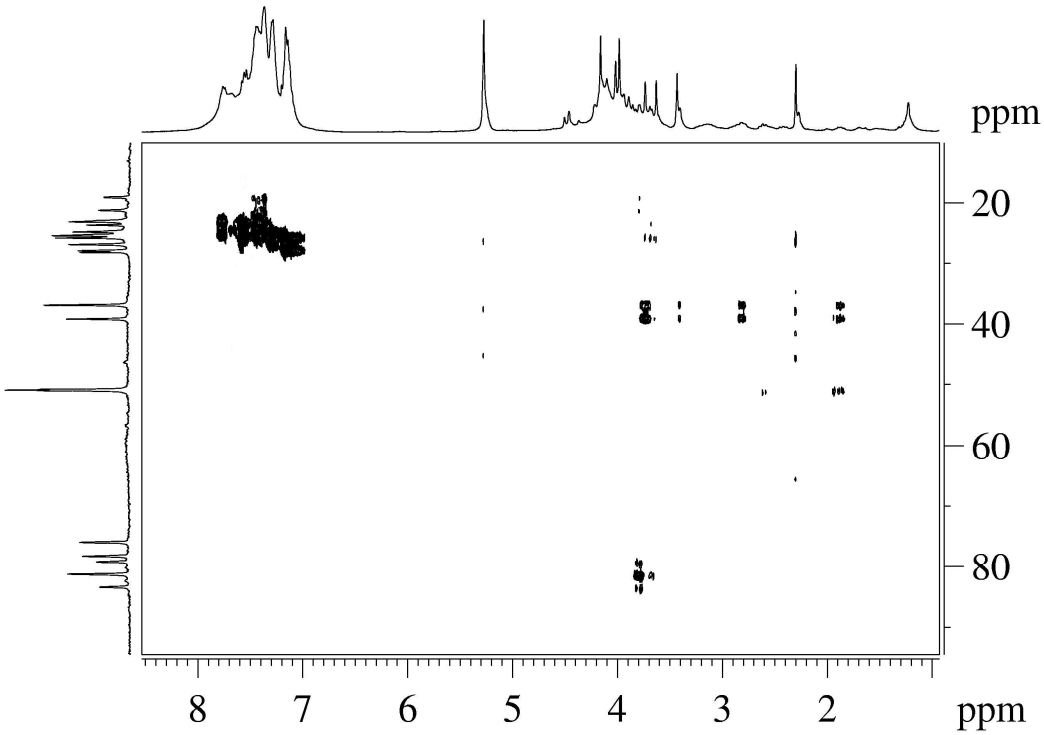


Figure S20: ^{1}H-^{31}P HMBC spectrum of **4a** and **4b** (CD_2Cl_2, 295 K)

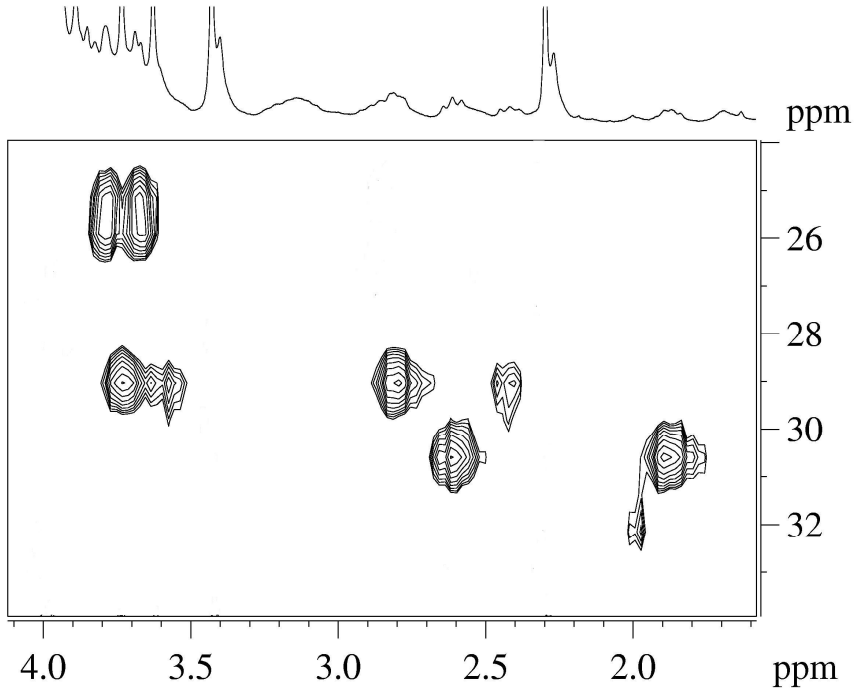


Figure S21: Methylenic region of the ^{1}H-^{13}C-HMQC spectrum of **4a** and **4b** (CD_2Cl_2, 295 K)

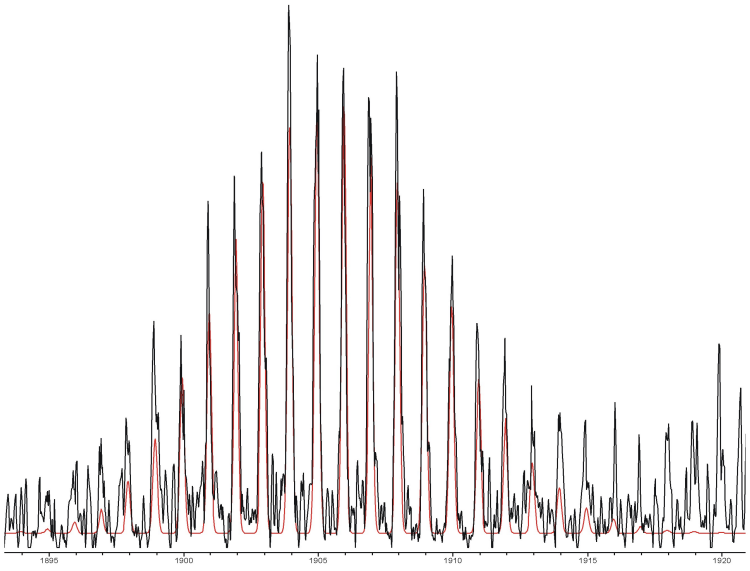


Figure S22: Experimental (black line) and simulated (red line) HRMS(+) spectrum of **4a** and **4b** (exact mass = 1901.8977 da) in THF diluted with CH_3CN. The error between simulated and observed isotopic patterns is 6.8 ppm.

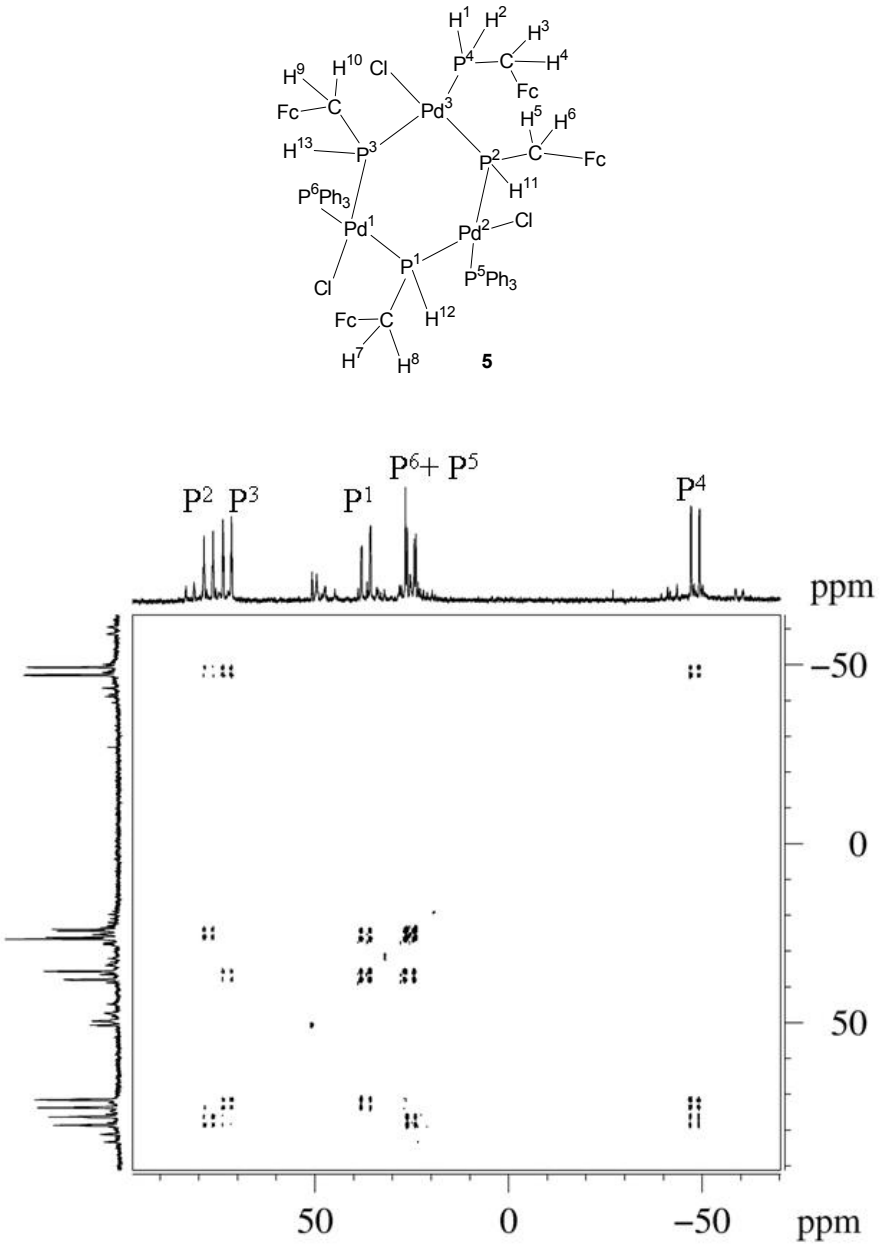


Figure S23: $^{31}P\{^{1}H\}$-COSY spectrum (CD_2Cl_2, 295 K) of **5**.

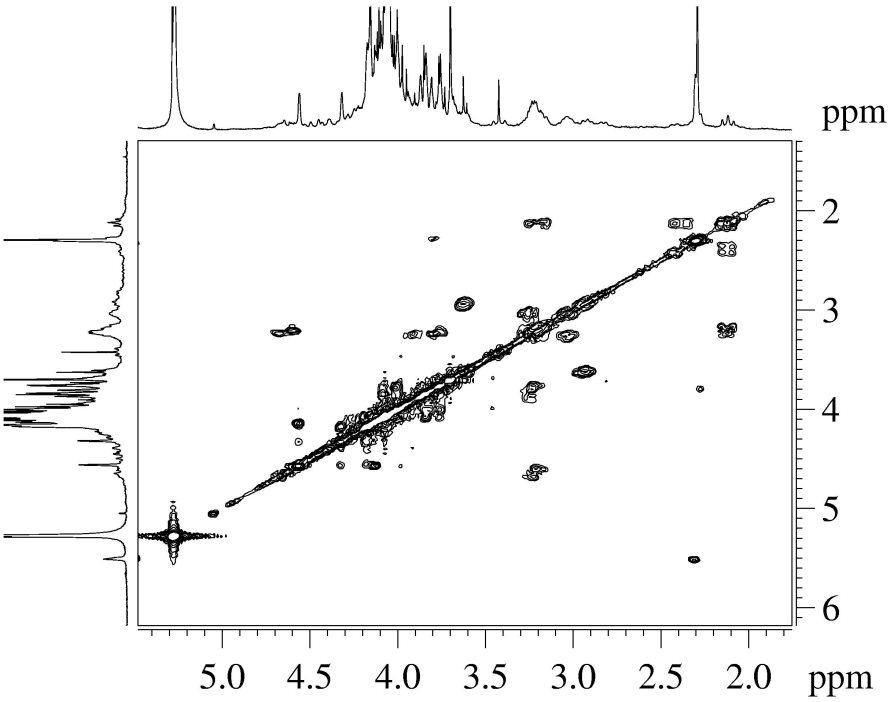


Figure S24: Portion of ^{1}H-COSY spectrum of **5** (CD_2Cl_2, 295 K).

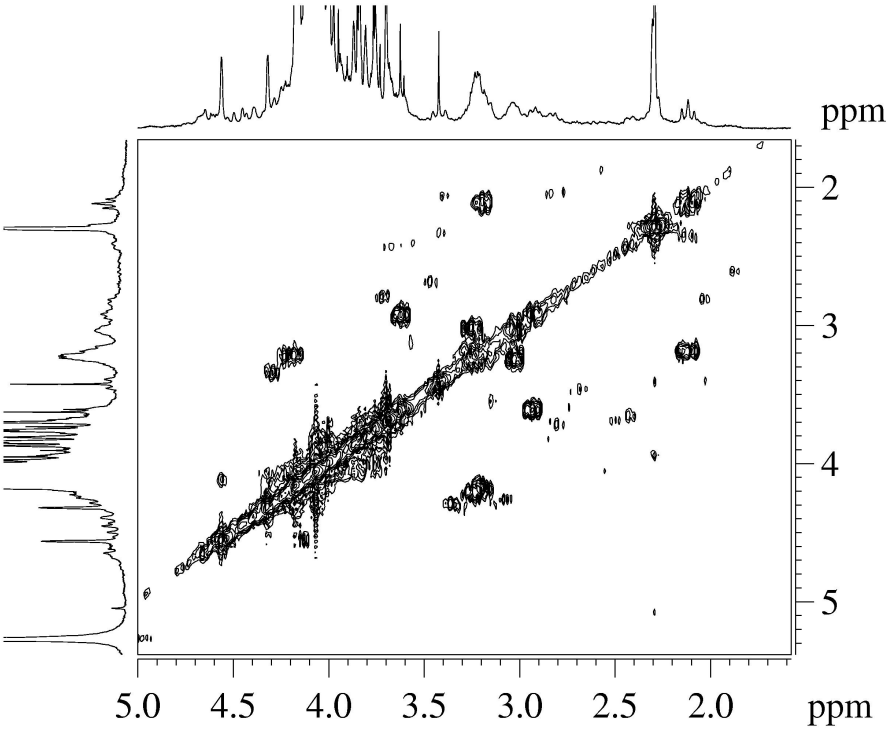


Figure S25: Portion of $^{1}H\{^{31}P\}$-COSY spectrum of **5** (CD_2Cl_2, 295 K).

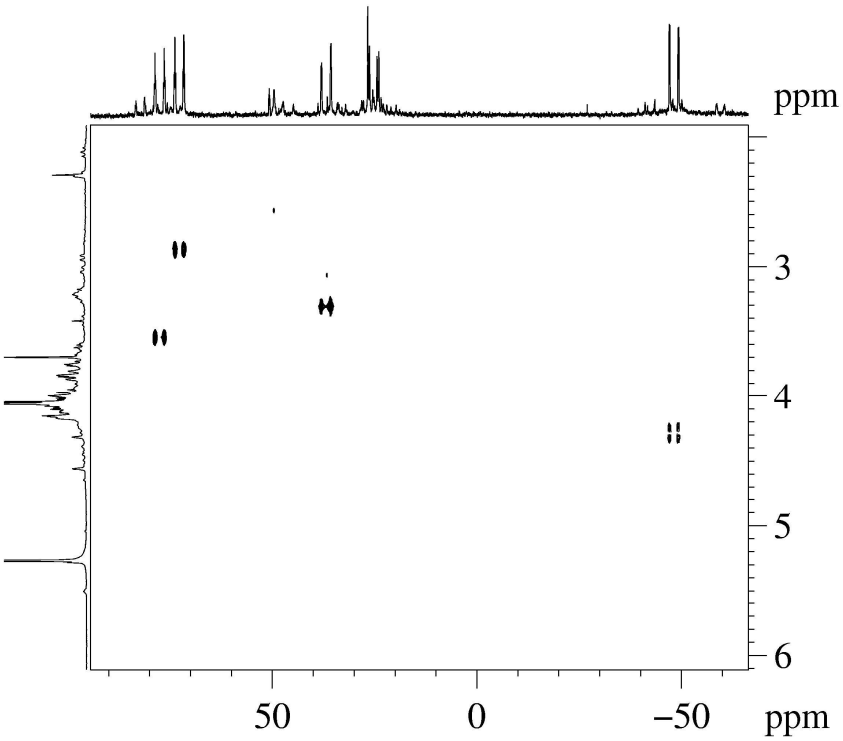


Figure S26: ^{31}P-^{1}H HETCOR spectrum of **5** (CD_2Cl_2, 295 K). The projection in F1 is the $^{1}H\{^{31}P\}$ NMR spectrum.

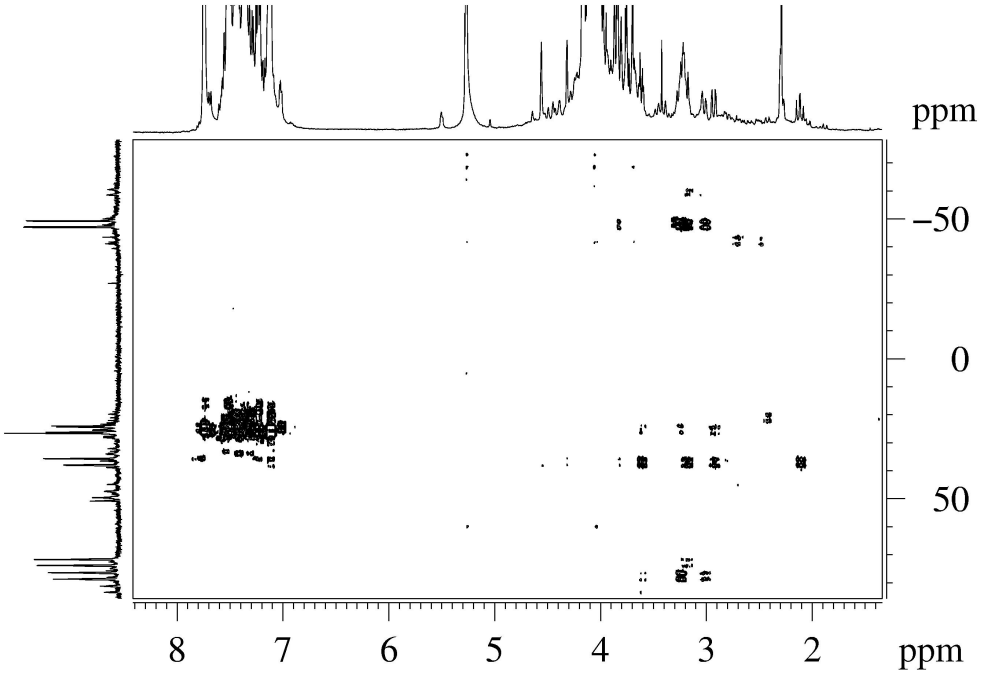


Figure S27: ^{1}H-^{31}P HMBC spectrum of **5** (CD_2Cl_2, 295 K)

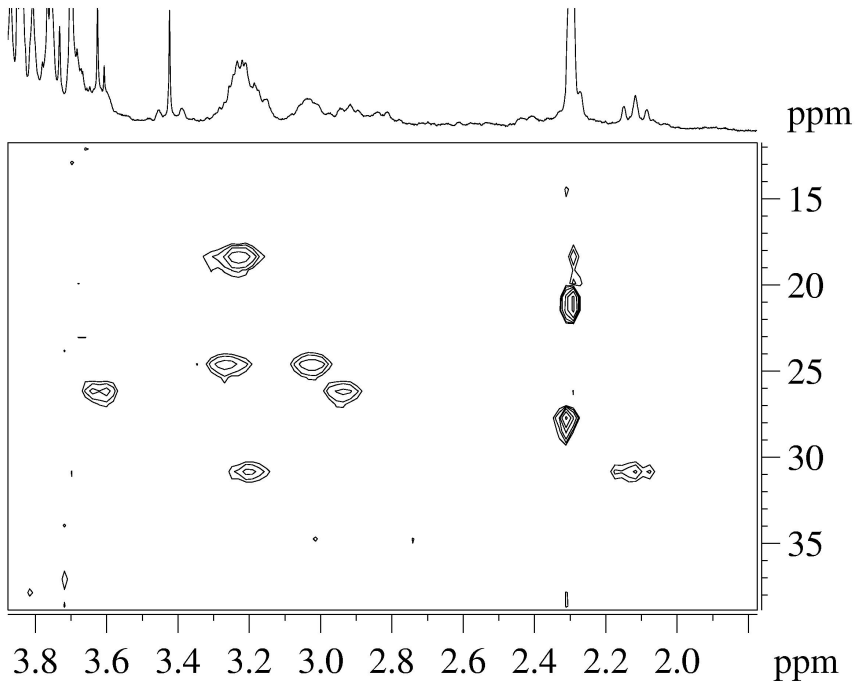


Figure S28: portion of ^{1}H-^{13}C HMQC spectrum of **5** (CD_2Cl_2, 295 K): methylene region.

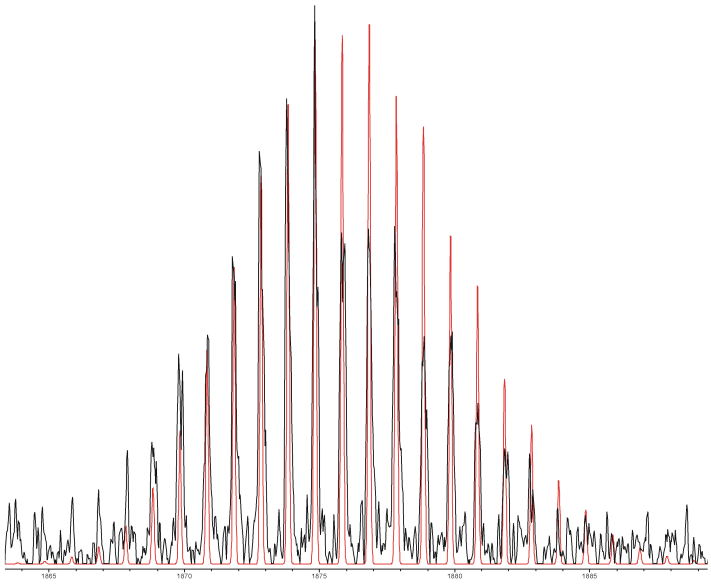
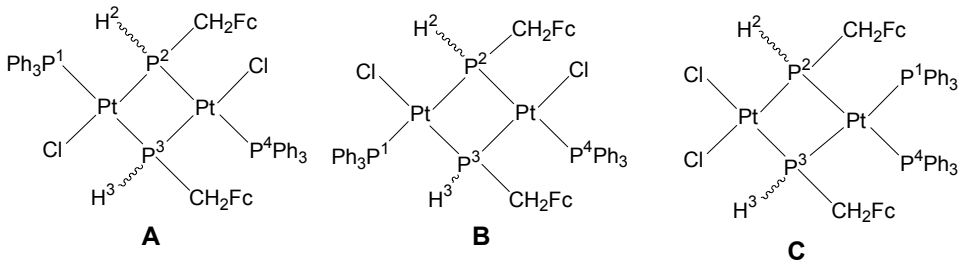
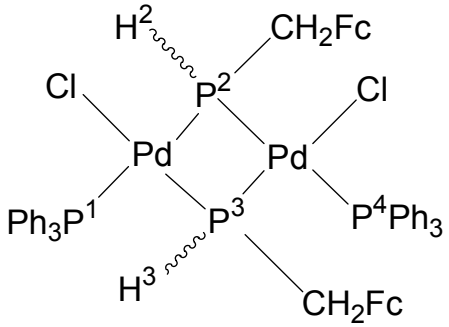


Figure S29: Experimental (black line) and simulated (red line) HRMS(+) spectrum of **5** (exact mass = 1871.8175 da) in THF diluted with CH_3CN. The error between simulated and observed isotopic patterns is 3.5 ppm.



	P(1)	P(2)	P(3)	P(4)	H(2)	H(3)
P(1)	**22.9** **23.8** **23.7**	5.0 348 7.9	385.9 - 382.0	- - -	- - -	- - -
P(2)		**–173.4** **–181.7** **–190.0**	179.6 180.0 183.9	385.9 348.0 382.0	300 357 340	- - -
P(3)			**–173.4** **–164.7** **–190.0**	5.0 - 7.9	- - -	300 360 340
P(4)				**22.9** **23.8** **23.7**	- - -	- - -
H(2)					**1.51** **3.72** **2.04**	- - -
H(3)						**1.51** **0.05** **2.04**

Table S1. ^{31}P and ^{1}H NMR parameters for complexes **A** (top), **B** (middle), and **C** (bottom), deriving from PPh_3 addition to **2**. (C_6D_6, 295 K, 162 MHz); chemical shifts (bold) are in ppm; coupling constants (normal) are in Hz.



D

	P(1)	**P(2)**	**P(3)**	**P(4)**	**H(2)**	**H(3)**
P(1)	**18.6**	355	-	-	-	-
P(2)		**–147.7**	245	355	355	-
P(3)			**–91.6**	-	-	351
P(4)				**18.6**	-	-
H(2)					**3.06**	-
H(3)						**3.70**

Table S2. ^{31}P and ^{1}H NMR parameters for complex **D** (CD_2Cl_2, 295 K, 162 MHz); chemical shifts (bold) are in ppm; coupling constants (normal) are in Hz.